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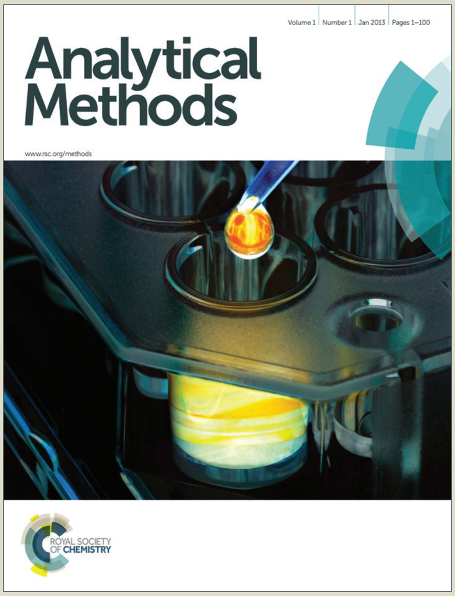

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/methods

Journal Name RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x
Received 00th January 2012,
Accepted 00th January 2012
DOI: 10.1039/x0xx00000x
www.rsc.org/

An electrochemical analyzer for *in situ* flow determinations of Pb(II) and Cd(II) in lake water with on-line data transmission and a global positing system

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An electrochemical analyzer based on a potentiostat/galvanostat (PG004) was developed and applied to perform *in situ* Pb^{2+} and Cd^{2+} determination in water samples with on-line data transmission, and a global positing system (GPS) to acquire the geographical coordinate of the place being monitored. For this, a flow-batch analysis (FBA) and a thermostated electrochemical flow cell (EFC) coupled with a boron-doped diamond electrode (BDD) were developed to measure these ions by employing square-wave anodic stripping voltammetry (SWASV). To study the Pb^{2+} and Cd^{2+} ions by *in situ* analysis, mainly for temperature variation, the PG004 was evaluated and the limits of detection were 0.08 µg L^{-1} and 0.18 µg L^{-1}, respectively, for simultaneous analysis. Then, the PG004 was used for *in situ* determinations of analytes in lake water samples, and voltammograms with good resolution and low noisy were obtained. Recoveries ranged from 93.3% to 109%, and waste generated as low as 700 µL per determination were acquired. The accuracy of the method was checked by determination of Cd^{2+} and Pb^{2+} in certified water (NIST), and *t*-unpaired test was applied for $n = 3$, and values found were in close agreement at a confidence level of 95%. Besides the geographical coordinates obtained by using a GPS receiver, and experimental data sent via wireless, the device used a solar board as renewable energy. The developed system proved to be a useful tool to measure Pb^{2+} and Cd^{2+} in lake samples with a fast, on-line, and environmentally friendly analytical method.

Introduction

Water is a natural resource of great importance in various economic sectors, such as industry and agriculture, and also for the world population, which is constantly growing. The uncontrolled population growth coupled with reckless practices in activities, such as agriculture, mineral exploration, and industry, has led to the contamination of air and soil, and consequently to the pollution of the water, particularly groundwater, which is a global problem.[1-3] Moreover, toxic metal ions and organic compounds are released into the waters, polluting even the sources of rivers and lakes.[4,5] In fact, many cases of contamination of different ecosystems with high concentrations of metals in the habitat and throughout the food chain[6-10] have been reported[4, 11-15].

Metal ions, such as Pb^{2+} and Cd^{2+}, have toxic properties, and act as pollutants with carcinogenic potential. Both metal ions are bioaccumulative, thus propagating along the food chain due to poor elimination by the organisms that cannot efficiently metabolize or excrete them.[11-16] These ions can reach the bloodstream in humans and are easily absorbed by kidney, liver, and bone.[17-19] Several governmental agencies regulate the maximum levels of metals ions to establish water quality standards. For some kinds of fresh water, the tolerable concentrations of Cd^{2+} and Pb^{2+} are 1.0 and 10 µg L^{-1}, respectively.[18,20] However, in many countries, especially in developing countries, technologies that allow the real-time and *in situ* analysis of these metallic ions are limited.

Currently, the time required to perform the full analysis of pollutants in the water of rivers and lakes usually takes hours or even days.[4] Indeed, difficulties in arriving at the place under study to obtain representative samples, bringing them to the laboratory, and performing analysis is a laborious and costly task that requires long times. Because of this, contamination of a water body can take days to be observed or detected, and thus the problem may advance, leading to irreversible environmental damage. In addition, handling of samples can lead to serious analytical errors by contamination and loss of analytes due to changes in physical-chemical and microbiological properties of the samples. These problems can be avoided employing *in situ* analysis and data transmission in real-time. In this context, the use of wireless network for analytical data transmission is essential to perform a fast decision or to send alerts about contamination to environmental protect agencies.[21] Thus, these agencies can explore this technique to monitor the water sources making a decision to prevent environmental disaster such as petroleum spill or disposal of industrial effluents employing several wireless techniques.[22]

There are several models of potentiostats/galvanostats (PGs) commercially available for industry and research. However, most require a stable electricity source to operate and/or present poor portability, which hampers their use for *in situ* environmental analysis. From those few that are portable equipment, none of them are able to perform wireless data transmission, and they do not allow a precise location of the geographic coordinates to be known, which is essential to ensure traceability of the water samples. Other features, such as the flow analysis approach, required for a high-throughput analysis and the thermostatic control of the samples during *in situ* measurements is not currently available in commercial PGs.[23] Thus, lab-made electrochemical analyzers were developed to overcome some of these drawbacks.[21, 24-28]

Thermostated control coupled to flow analysis can lead to more reproducible, accurate, and precise results, since the variation in temperature during *in situ* measurements strongly changes the electrochemical responses.[29] Moreover, aiming to reduce the waste generated, the use of miniaturized electrodes is a good alternative,[30] particularly when they are coupled to an electrochemical flow cell in which only a few microliters are used.[23]

Electrodes for environmental application should present high chemical inertness, low adsorption, low residual current, high insensitivity to dissolved oxygen, with a wide work potential window, and high overpotentials for H_2(g) and O_2(g). Boron-doped diamond electrode (BDD) presents all features described previously, being used for several applications[31-33] and potentially useful for in situ analysis.[34]

In order to meet the requirements described, a portable PG and a BDD electrode coupled to a thermostated electrochemical flow cell for *in situ* determinations of Pb(II) and Cd(II) in lake water samples with on-line data transmission is presented. For this, wireless communication based on Wi-Fi, Bluetooth, and GPRS (General Packet Radio Service) were used for data transmission, as well as GPS (Global Positioning System) to get geographic coordinates. Additionally, the PG was designed to use solar plates as a clean and renewable energy source useful for environmental application.

Experimental

Apparatus and instrumentation

The potentiostat/galvanostat models PG581 (Uniscan, England) and PAR 173A (Princeton Applied Research, USA) were used for comparative tests. Multimeter models 3458A and 3478A (Agilent, USA), and an oscilloscope (Tektronix, USA), model MSO2024 were employed.

An integrated Wi-Fi and Bluetooth mini-board (Atheros, USA), model AR9002WB-1NG (54 Mb/s - 802.11g, 128 bits, WPA), and a XEB 33-416/LF motherboard with Atom N270 (Intel, USA) as a central processing unit (CPU), was used. A PWR/ATX-M2 board (Cortex, Brazil), a ME2000RW GPS receiver (ME, Brazil), a 3G modem (Cortex, Brazil), a XTS-080/4W 8 inches touchscreen (Cortex, Brazil), a 2Gb/667MHz RAM memory (Kingston, USA), and a 60Gb hard disk (OCZ, USA) were used.

For the flow system, an actuator controlled by a 6211 USB interface (NI, USA) and software programmed in LabView (NI, USA) were used to drive the solenoid micropumps (µP), models 120SP1250-4EE and 120SP1220-4EE (Coleparmer, USA) and the three-way solenoid valves (SV) (Neptune Research, USA) model 161TO31. Polypropylene tubes with 0.8 mm i.d were used in the flow system.

To construct a thermostated electrochemical flow cell, a microcontrolled board was used to control a Peltier thermoelectric cell (Danvic, Brazil); model HTC-40-03-15.4, and an LM35 temperature sensor (Texas Instruments, USA). As a power supply, rechargeable batteries of 12 V with 7 A h^{-1} (Unipower, Brazil) were used. Moreover, solar plates of 20 W (18 W, 1.11 A) and 5 W (18 W, 0.28 A) were also employed.

A BDD (8000 ppm boron) was used as the working electrode (WE), which was acquired from the Centre Suisse Electronique et de Microtechnique SA (Switzerland). The pseudo-reference electrode (Pseudo-RE) and counter electrode (CE) were produced using a conductive silver epoxy resin and a graphite ink (Electron Microscopy Sciences, USA), respectively. Printed circuit boards (PCB) were used to construct the electrodes.

Chemicals and samples

A 0.2 mol L^{-1} acetic acid/acetate buffer solution, pH 4.0, and a stock solution of 0.1 mol L^{-1} H_2SO_4 were used. A solution of 1.0×10^{-3} mol L^{-1} potassium hexacyanoferrate (III) in 1.0 mol L^{-1} KCl was used. Solutions of certified metal ions from the National Institute of Standards and Technology (NIST, USA), 1000 mg L^{-1} of Pb^{2+} and Cd^{2+} dissolved in 0.1 mol L^{-1} HNO_3, were purchased from Merck (Germany), and diluted with acetic acid/acetate (0.2 mol L^{-1}) solution. Deionized water (resistivity > 1.8 MΩ•cm) from a Milli-Q system (Millipore, USA) was used. A certified water (1643e Trace Elements in Water, NIST) with 19.63 ± 0.21 µg L^{-1} and 6.57 ± 0.073 µg L^{-1} for Pb^{2+} and Cd^{2+} ions was used. The water samples were pumped using the micropumps of the PG004 from the Dam of Monjolinho Lake in São Carlos (Brazil) at three distinct locations ((1) 21°59.1655'S; 47°52.9343'W; (2) 21°59.1203'S; 47°52.9038'W, and (3) 21°59.1763'S; 47°52.8790'W), and in-line filtered using disposable syringe filters composed of a PTFE (polytetrafluoroethylene) disc of 0.45 µm porosity (Whatman, USA).

Construction of Potentiostat/galvanostat

The potentiostat/galvanostat was designed to perform the following functions: (1) control of potential or current; (2) flow analysis procedure; (3) thermostated control; and (4) wireless data transmission and tracking of geographical coordinates with a GPS receiver. Due to these four main functions, the instrument was named PG004 (Fig. 1).

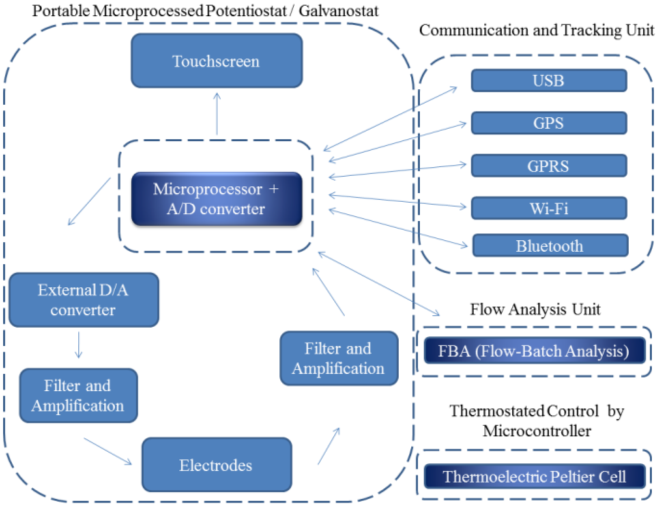

Fig. 1. Block diagram of the potentiostat/galvanostat with communication and tracking unit, flow analysis, and thermostated control unit.

According to Fig. 1, the microprocessed CPU sends a digital signal to a D/A (digital/analog) converter, through an interface, and then this signal is amplified and filtered, to stimulate the electrodes, after, an electrical current is recorded. However, an amplification and subsequent filtering of the signals produced is required. Finally, the analog/digital (A/D) conversion is performed. By using the touchscreen, all functions of the PG004 can be accessed. In addition, the CPU controls the GPS receiver, Wi-Fi and Bluetooth board, 3G modem, USB, and flow system. The thermostated control was carried out using a microcontrolled board driven by software in C language.[29]

Figure S1 in Electronic Supplementary Information (ESI) presents the basic electronic circuits of the PG004.[35,36]

For the performance test, the solar plates of 20 W (18 V, 1.11 A) and 5 W (18 V, 0.28 A) were installed, directed in sunlight, and were used to charge the 12 V with 7 A h^{-1} lead-acid batteries used. To check the loading efficiency of batteries, a microcontrolled board (Land Star, USA) was used.

Communication module and data transmission

For *in situ* analysis employing the PG004, the data were sent via the internet using a Wi-Fi tower located within 300 m at a transmission rate of 54 Mb/s. In the absence of this type of signal, GPRS employing a 3G modem was used. For a short distance, e.g. up to 10 m, Bluetooth was employed between the PG004 and a smartphone (GT S5360B, Samsung). The GPS receiver was operated at a frequency of 1.3 GHz. The geographic coordinates were acquired by synchronization of seven satellites, providing an accuracy of 5 m. The wireless peripherals managed by PG004 are shown in Fig. S2.

The screen-printed electrode and flow analysis system

Aiming to reduce the chemical consumption and the waste generated, and allowing a fully automated electrochemical control for *in situ* analyses, a screen-printed electrode (SPE) with a coupled boron-doped diamond (SPE-BDD) was used in a thermostated electrochemical flow cell. Experimental details of the construction of the SPE-BDD and the materials used have been reported in previous work,[37] as well as the surface characterization of the used commercial BDD.[33] On the other hand, due to the use of a commercial (Dropsens, USA) screen-printed graphite carbon electrode (SPCE), which was only used to evaluate the PG004 performance, a new model of the EFC was specifically developed, Fig. 2.

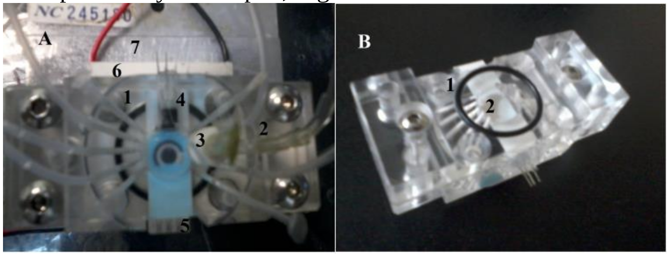

Fig. 2. A SPCE coupled to a EFC (A), with 1: 0.8 mm i.d. inlet flow (eight), 2: 3.0 mm outlet flow, 3: an optional connection to a RE, 4: temperature sensor, 5: connection to PG004, 6: thermoelectric cell, 7: heatsink. Bottom of the EFC (B), with 1: a 2.1 cm i.d. thermoplastic O-ring, 2: reduction from 0.8 mm i.d. to 0.05 mm i.d. to prevent each tube crossing the EFC.

In this new model of the EFC, the inner chamber had a height of 8.0 mm, and an inner radius of 5.5 mm, which kept the internal volume at 700 µL, including the volume occupied by the SPCE, a magnetic bar, and a temperature sensor. A silicone film was used in the region near the electrical contacts of the SPCE as reinforcement to seal it. Thus, this new EFC was employed with a SPCE to measure a $K_3[Fe(CN)_6]$ solution used as reference in electrochemical studies.

Potentiostat/Galvanostat PG004

According to Fig. 3, the flow module was physically separated from the PG004. However, the commands from the flow module were controlled by the CPU of PG004 via the interface.

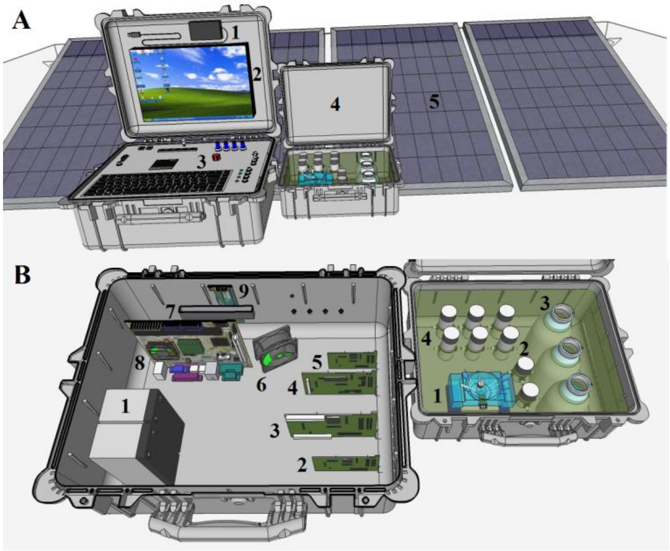

Fig. 3. The PG004 (A), 1: GPS, 2: touchscreen, 3: panel with an optional keyboard, keys, and command bottoms, 4: flow module, 5: solar boards. The internal view of the PG004 (B), 1: 12 V batteries, 2: actuator of the flow system, 3: galvanostat board, 4: potentiostat board, 5: thermostated control, 6: fan, 7: USB hub, 8: CPU, 9: microcontrolled board to control the batteries. The Wi-Fi and Bluetooth board is inserted in the CPU. Flow module, with 1: EFC, 2: SVs, 3: solutions compartment, 4: µPs.

In the panel of the PG004 are also present all the connectors for the apparatus of the flow unit and the thermostated control module, e.g., micropumps and solenoid valves, stirrer, Peltier cell, fan, temperature sensor, electrode cables, and a switch to select the potentiostat or galvanostat function. The operational system used was Windows (Microsoft, USA), but it can operate using other operational systems compatible with the LabView platform used to control the PG004. For more details of the PG004, an illustrated video in AVI format is supplied as ESI.

Calibration, precision, and accuracy tests of the PG004

For the calibration of the PG004 an oscilloscope and amperimeter were used. After these calibrations, the performance of the PG004 was compared to commercial PGs using $K_3[Fe(CN)_6]$ solutions. Moreover, to check the repeatability (four successive measurements), and the reproducibility (three measurements along the working day) at intervals of 6 h, analyses with SWASV for Cd^{2+} determination was carried out. To perform these procedures, 240 µL of a stock solution of 220.3 µg L^{-1} Cd^{2+} were inserted in the EFC by switching ON the μP_3. The remaining volume, i.e, 460 µL, was completed with supporting electrolyte (acetic acid/acetate buffer, pH 4.0) by μP_1 with trigger activation of SV_1 and stirrer.

To certify the accuracy of the method, certified water (1643e Trace Elements in Water, NIST) with 19.63 ± 0.21 µg L^{-1} and

6.57 ± 0.073 μg L^{-1} for Pb^{2+} and Cd^{2+} ions respectively was used. The experiments were carried out at a controlled temperature of 25ºC ± 1°C.

Using the PG004 for *in situ* analysis

For *in situ* analysis, the PG004 was moved to the field, and the geographic coordinates were acquired by the GPS receiver. Next, using the μP_5, aliquots of water samples were pumped and in-line filtered using a disposable 0.45 μm PTFE filter positioned along the flow tubes. At the same time, all the flow channels were filled with the respective solutions, according to the flow-batch analysis (FBA) manifold presented in Fig. 4. To determine Pb^{2+} and Cd^{2+} ions, the SPE-BDD was employed, but a pretreatment of the BDD surface was previously carried out.[37]

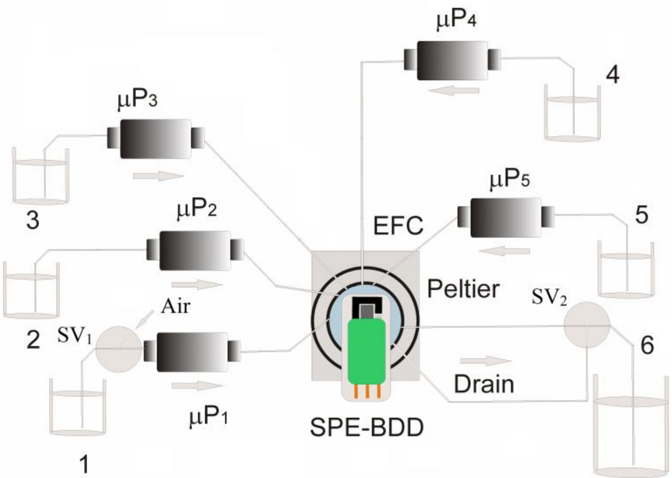

Fig. 4. FBA manifold developed. The μP_1, μP_4, and μP_5 were used to pump 50 μL per pulse of acetic acid/acetate buffer solution, pH 4.0 (1), 0.1 mol L^{-1} H_2SO_4 (4), and samples (5), respectively. The μP_2 and μP_3 pump 20 μL per pulse of the stock solutions of Pb^{2+} (2) and Cd^{2+} (3). SV_1 and SV_2 are the three-way solenoid valves and the waste (6), respectively.

The anodic and cathodic pretreatment of the BDD were carried out employing +50 mA/cm^2 for 60 s and −50 mA/cm^2 for 120 s, respectively, by chronopotentiometry using a 0.1 mol L^{-1} H_2SO_4 solution.[37] Subsequently, the method of standard addition using the FBA approach was performed to detect Pb^{2+} and Cd^{2+} by SWASV (square-wave anodic stripping voltammetry) at a controlled temperature of 25ºC ± 1°C. Finally, the data were stored in peripherals (*e.g.* flash drive or external hard drive), and sent to a smartphone via Bluetooth or to a server computer via the internet employing the GPRS with 3G modem. The Wi-Fi was not employed for this purpose due to its short range of 300 m.

Result and discussion

Solar plate test

With the solar plate of 20 W, the rechargeable batteries (12 V with 7 A h^{-1}) were charged in about 4 h. Thus, the solar plates provide good performance to charge batteries for *in situ* applications. Thus, according to power consumption, the PG can operate for 18 h in potentiostat mode, and approximately 6 h in galvanostat mode.

Evaluation of the developed software

To perform the validation of the developed software in LabView to control the PG004, the commercial PG model 173A was employed, and the analog signals generated were measured using the oscilloscope. The electrochemical data were acquired by measurements of a 1.0 × 10^{-3} mol L^{-1} potassium hexacyanoferrate (III) solution in 1.0 mol L^{-1} KCl using the SPCE. Fig. S3 and S4 show the results simultaneously obtained by the PG and by the oscilloscope, respectively. To control the galvanostat, a similar procedure was carried out. The data obtained using chronopotentiometry for the pretreatment of the BDD electrode are shown in Fig. S5 (A) and (B).

Performance tests employing the PG004

The potentiostat PG581 (Uniscan, England) is portable and has technical specifications that are similar to the PG004, and thus, it was used for comparison purposes. According to the acquired data (Fig. S6), no significant differences in peak current, peak potential, or profiles of the voltammograms were observed between instruments. PG004 presented good repeatability with RSD of 2.75%, 2.83%, and 1.01% for DPV, CV, and SWV, respectively, for 1.0 × 10^{-3} mol L^{-1} potassium hexacyanoferrate (III) solution in 1.0 mol L^{-1} KCl, using the SPE-BDD.

The repeatability and reproducibility obtained using the SWASV to determine with Cd^{2+} ions were 1.08% (n = 4) and 7.50% (n = 3), respectively, with a sampling frequency of 30 determinations per hour.

To accuracy assays, concentrations of 19.0 ± 0.6 μg L^{-1} and 6.7 ± 0.4 μg L^{-1} for Pb^{2+} and Cd^{2+} ions were found by interpolation in an analytical curve. The *t*-unpaired test was applied for n = 3, and values found were 1.48 and 0.42 for Pb^{2+} and Cd^{2+} ions respectively, which are in very close agreement at a confidence level of 95%, *t*-test (2, 95%). These results confirm the good performance of the developed PG004.

Wi-Fi transmission employing the PG004

The electrochemical data of cyclic voltammetry in txt format (772 Kb) were sent by the PG004 to a server computer located in the industry (FAC, Brazil), based on the transmission communication protocol (TCP) for the internet protocol (IP) (TCP/IP), as described in Fig. S7. Once the communication was established, the data were sent using the respective IP addresses of the PG004 and the server computer. Using Wi-Fi communication, the on-line experiment data were quickly obtained and evaluated in real time.

Simulation of *in situ* temperature employing the PG004

Previous tests performed in the laboratory to simulate temperature variation during *in situ* determination were carried out. The laboratory acclimatization system was switched OFF and the supporting electrolyte was injected into the EFC at temperatures ranging from 15ºC to 45°C.[23] Thus, the PG004 was used to construct analytical curves for Pb^{2+} and Cd^{2+} ions, alone or simultaneous determination, by employing the SPE-BDD with the FBA approach using SWASV. For this, the appropriate pulses of μP_2 and μP_3 were applied to add stock solutions into the EFC, as well as supporting electrolyte by activating μP_1 triggered with SV_1. Furthermore, the thermostated EFC was used for heating (T ≤ 24°C) or cooling (T ≥ 26°C) in situations where the temperature (T) of the solution or sample was outside the range of 25ºC ± 1°C. The analytical curves obtained are presented in Fig. 5.

Well-defined voltammograms, with good resolution and no noise, were obtained with the PG004 operating via the battery module with a good correlation between peak current and concentration of each analyte, independently of whether single or simultaneous analyses were performed. Table 1 shows the data obtained regarding the performance of the PG004.

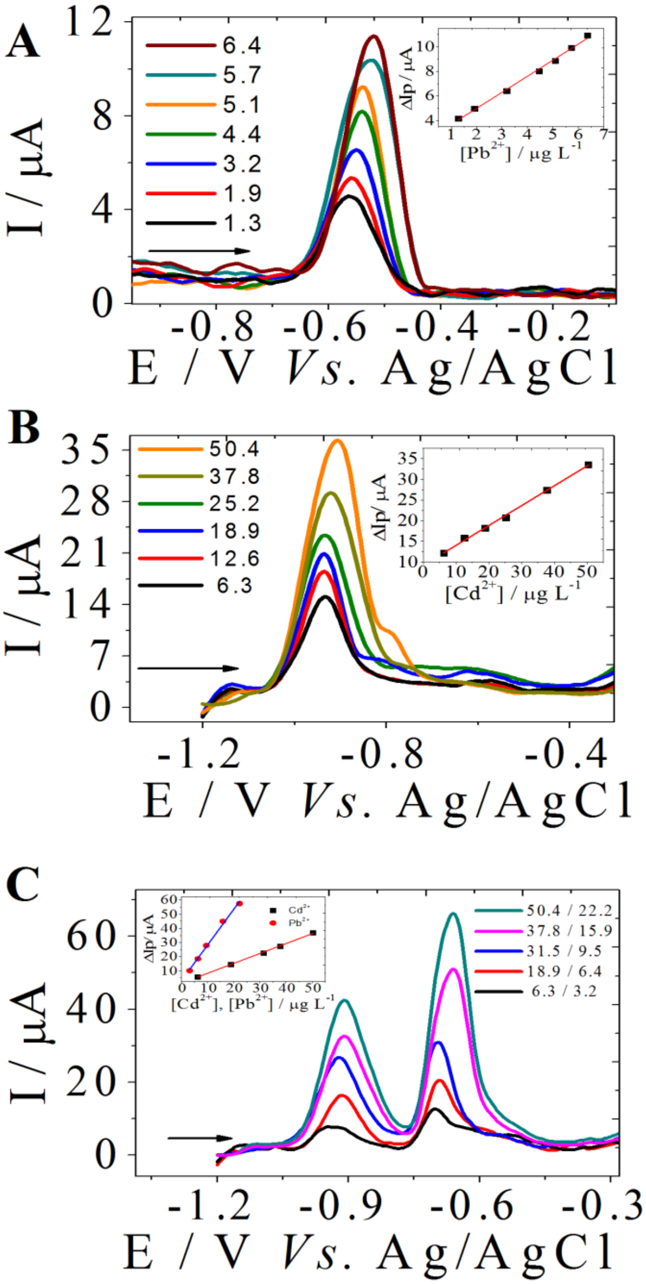

Fig. 5. Analytical curve employing SWASV for the determination of Pb^{2+} (A) and Cd^{2+} (B) for single or simultaneous determination (C). SWASV: potential and time of deposition were -1.4 V and 60 s respectively, with ΔE: 5 mV, f: 30 Hz, a: 100 mV.

As presented in Table 1, the PG004 allowed obtaining low LDs and LQs with appreciable linear ranges, mainly for the simultaneous determination. Moreover, good repeatability was obtained at a sampling frequency of 30 determinations per hour.

Studies of interference were carried out during the determination of Pb^{2+} and Cd^{2+} ions in water of lake containing Li^+, Na^+, K^+, Mg^{2+}, Cu^{2+}, Hg^{2+}, Ca^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, NO^{3-}, Cl^-, SO_4^{2-}, PO_4^{3-}, and humic acid. Among all substances evaluated, only humic acid in concentration of 0.01% (m/v), and Cu^{2+} and Hg^{2+} in 1:1 ratio (analyte: interferent) presented interference around 10%.[37]

Table 1. The main results obtained using SPE-BDD with SWASV.

	Single determination		Simultaneous determination
^{a}P	Pb^{2+}	Cd^{2+}	$^{f}Cd^{2+}$ / Pb^{2+}
^{b}S	1.24	0.48	0.70 / 2.52
^{c}r	0.991	0.997	0.990 / 0.993
LD	0.18	0.50	0.18 / 0.08
LQ	0.59	1.70	0.59 / 0.27
^{d}LR	1.30 – 6.40	6.30 – 50.4	6.30 – 50.4 / 3.20 – 22.2
^{e}Rep	4.1% / 3.20	1.5% / 25.2	3.2% / 18.9 3.7% / 6.40

^{a}Parameters of the analytical performance. ^{b}Analytical sensitivity in μA / μg L^{-1}. ^{c}Coefficient of linear regression. ^{d}Linear range in μg L^{-1}. ^{e}RSD with n = 3 / analyte concentration in μg L^{-1}. ^{f}Simultaneous determination of Pb^{2+} and Cd^{2+}, and the results obtained for each metal ion separated by "/".

In situ analyses employing the PG004

The samples were pumped towards the EFC by employing μP$_5$, followed by in-line filtering using a 0.45 μm filter inserted into the transmission line of the FBA system. The surface water temperature ranged from 20ºC to 27°C during the working day at the Dam of Monjolinho Lake. Aliquots of 100 and 200 μL of the samples were injected into the EFC, and were kept at 25ºC ± 1°C using the thermostated system. Then, recovery tests were performed to accomplish the quantification of Pb^{2+} and Cd^{2+} in single or simultaneous modes. For this, SWASV was performed using the SPE-BDD and the PG004. Previously, the concentrations of Cd^{2+} and Pb^{2+} ions in samples were analyzed by ICP-MS and concentrations were below of the LDs, lower than 0.05 and 0.08 μg L^{-1} respectively. Because of this, the recovery testes were employed in electrochemical method. Photographs regarding *in situ* analysis of Pb^{2+} and Cd^{2+} in samples of water from the Dam of Monjolinho Lake, located using the GPS data receiver, are shown in Fig. S8, with the main results shown in Table 2.

Table 2. *In situ* determination of Pb^{2+} and Cd^{2+} for single and simultaneous determination using the recovery method.

	Added/ μg L^{-1}		Found / μg L^{-1}		Recovery / %	
^{a}A	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	$^{b}R_1$	$^{b}R_2$
A1	6.3	3.2	6.4 ± 0.6	3.5 ± 0.2	101	109
A2	12.6	4.4	12.3 ± 0.2	4.7 ± 0.9	97.8	107
A3	18.9	6.4	19.8 ± 0.4	5.9 ± 0.8	105	93.3
^{c}A4	12.6	3.2	12.6 ± 0.4	3.3 ± 0.5	100	103
^{c}A5	25.2	9.5	24.3 ± 0.2	9.2 ± 0.7	96.4	96.8

^{a}Sample, ^{b}Recovery for Cd^{2+} and Pb^{2+} ions, with n = 3. ^{c}Simultaneous determination.

As presented in Table 2, recoveries ranging from 93.3% to 109% with low standard deviations were acquired, even when subjected to environmental temperature variations, since the PG004 presents an efficient thermostated system. In addition, solar boards provided great energy autonomy, considering that the *in situ* analysis took approximately 8 h, the batteries were recharged without any interruption in the power supply of the PG004. Moreover, low levels of waste, i.e., 700 μL, were generated per determination, with the residues being properly stored and taken to the waste management unit (UFSCar, Brazil). Between the samples analysis, the filters were changed as well as the 0.8 mm i.d polypropylene tubes used to acquisition of the sample to avoid contamination.

Comparison of commercial PGs and the PG004

Table 3 present the main features of the PG004, commercialized and PGs described in the literature.

Table 3. Comparison among the PG004 and others PGs found in the market or in literature.

Features	[e]Ref.[38]	[e]Ref.[39]	[e]Ref.[40]	[e]Ref.[41]	µStat 400	µStat 200	DY 2100	PG581	PG004
Compliance / V	± 3.0	± 5.0	± 5.0	± 13	± 4.0	± 2.0	± 2.2	± 8.0	± 10.0
Resolution/ µV	± 200	± 125	± 76	± 1000	± 1000	± 5000	± 76	± 61	± 153
[a]Current/ mA	5	100	2	10	80	0.2	2	20	150
[b]Galvanostat	Yes	No	No	No	Yes	No	No	Yes	Yes
Automatic scale	5	No	4	No	8	6	6	8	No
External CPU	No	Yes	Yes	Yes	Yes	Yes	Yes	No	No
Communication	[f]RS/USB	USB	[f]RS/USB	No	USB/ Bluetooth	USB	USB	USB	USB/GPRS/GPS/ Bluetooth/Wi-Fi
[c]Thermostated	No	No	No	No	No	No	No	No	Yes
Flow analysis	Yes	No	No	No	No	No	No	No	Yes
[d]Internet	No	No	No	No	No	No	No	No	Yes
GPS	No	No	No	No	No	No	No	No	Yes

[a]Potentiostat/ mA, [b]Galvanostat module, [c]Thermostated control, [d]Data transmission using internet. [e]Literature. [f]RS232.

As presented in Table 3, the PG004 has different electric and technological features in relation to those found in the market and literature. The remarkable features of the PG004 are the higher electric current, i.e., 150 mA in the potentiostat mode, the versatility in data transmission, the thermostated control, the flow system, and the GPS data receiver. Moreover, among those models with the galvanostat mode, the PG004 has a higher electric current (up to 1.0 A). Thus, the PG004 has features that allow greater flexibility and automation of the analytical procedures, which is useful for *in situ* analysis.

Wireless data transmission for *in situ* analysis

The data acquired by *in situ* determination were sent by email using the 3G modem with GPRS technology at a transmission speed of 32 Kb/s. This procedure was preferable due to a wider coverage area than the Wi-Fi. Wireless data transmission using Bluetooth was also used in the PG004, in which a smartphone was placed up to 10 m away from it. Further, the data transmission of a DPV.txt file (2 Kb) generated by the PG004 was sent to the smartphone at a transmission rate of 101 Kb/s. The data were sent without oscillation in the transmission and with sufficient speed.

Moreover, information about the geographical coordinates of the sample under analysis was obtained from the GPS receiver. Fig. S9 shows the software that was developed in LabView to obtain the data from the GPS receiver using the National Marine Electronics Association (NMEA) navigation protocol,[42,43] NMEA-0183, version 3.01, at a rate of 9600 baud. As presented in Fig. S9, for the NMEA protocol, each line ports information such as number of satellites, latitude and longitude coordinates, time, date of transmission, among other information. Supported by this information, a complete record and geographical location of the *in situ* water samples was acquired using the PG004.

Conclusions

The PG004 showed good portability, low noise level, and low-power consumption. On-line data transmission using GPRS, Wi-Fi, and Bluetooth communication were satisfactorily performed, as well as the data acquisition of geographical coordinates using the GPS receiver. Furthermore, the thermostated EFC used in the FBA and the use of solar boards were important to perform a complete automation of the analytical procedure using a clean energy during the *in situ* analysis. The accuracy of the electrochemical method was checked for determination Cd^{2+} and Pb^{2+} in certified water, following the *t*-unpaired test was applied, and a very close agreement at a confidence level of 95% was found. Thus, based on the obtained results, the PG004 proved to be a useful instrument to rapidly determine Pb^{2+} and Cd^{2+} and/or eventually organic compounds (*e.g.* paraquat)[44] in lake water samples characterizing as an environmentally friendly method.

Acknowledgements

The authors acknowledge the CNPq, CAPES, and FAPESP, Proc. N° 2010/11690-0 and 2013/14993-1 for the financial support and scholarships supplied, and the FAC to the technological support and financial.

Notes and references

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Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/

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